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CHEMICAL AND ISOTOPIC VARIATIONS WITHIN THE

ORDOVICIAN KINNEKULLE A_1 BENTONITE, KINNEKULLE, SWEDEN

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF GEOLOGY

EDMONTON, ALBERTA

October, 1967

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the
Faculty of Graduate Studies for acceptance, a thesis entitled "Chemical and
Isotopic Variations within the Ordovician Kinnekulle A_1 Bentonite, Kinnekulle,
Sweden", submitted by Ngoc- Nga de la Cruz, B.Sc., in partial fulfilment of
the requirements for the degree of Master of Science.

ABSTRACT

Samples of biotite, sanidine, apatite and clay matrix from the Ordovician Kinnekulle A_1 bentonite at Kinnekulle, Sweden, were analysed for Rb and Sr by mass spectrometry and for Fe, Ti and K by X-ray fluorescence. Low and discordant Rb-Sr mineral dates were obtained ($\lambda = 1.47 \times 10^{-11} \text{ yr}^{-1}$). The biotite dates vary from 412 ± 12 m.y. to 305 ± 6 m.y. The "whole rock" date is 321 ± 12 m.y. while the clays yield dates down to 225 ± 12 m.y. Sanidine probably gives the time of deposition of the bentonite at 473 ± 32 m.y. Variations in the Rb-Sr content and ratio in the biotites depend to a certain extent on grain size. The biotites show no loss of iron or substantial change in Rb/K ratio with alteration, and the low Rb-Sr dates in any size group are similar. From the above information as well as the discordant U-Th-Pb dates of zircon from the bentonite, it is concluded that: (1) the pattern of chemical and isotopic variations in the biotite results from both diagenetic alteration and recent weathering; (2) the diagenetic alteration took place relatively early while recent weathering occurred in the last part of the post-depositional history of the bentonite; (3) bentonitic minerals are unsuitable for dating by the Rb-Sr method.

ACKNOWLEDGEMENTS

The writer is deeply indebted to Dr. H. Baadsgaard for his kind and patient supervision throughout the course of the present work.

Special thanks are due to Dr. R.E. Folinsbee and Dr. H. Baadsgaard for collecting the samples.

Mr. D. Green provided a computer program for Rb-Sr calculations and offered helpful comments on parts of the manuscript.

Mr. and Mrs. D. Tomlinson helped with the X-ray work and the Rb and Sr sample preparations. Mr. A. Stelmach analysed one sample for standardization. Mrs. M. Wylie typed the manuscript and Mrs. P. McIntyre the multilith masters. To them the writer wishes to express her appreciation.

Financial assistance in the form of a Research Assistantship was provided by the University of Alberta and through grants from the Geological Survey of Canada and the National Research Council of Canada.

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I - INTRODUCTION

Nature of study

Bentonite beds represent the altered and unaltered remains of pyroclastic sediments deposited in a relatively short period of geologic time. These sediments are often uncontaminated with normal detrital material, and furnish excellent stratigraphic marker horizons. Water-lain pyroclastic ash beds are commonly converted to mainly montmorillonitic clay beds containing more or less unaltered original minerals such as sanidine, zircon, plagioclase and biotite. Radiometric dating of unaltered sanidine, plagioclase and biotite often yield concordant K-Ar dates which are taken to be the time of deposition of the strata. On the other hand, little is certain about variations in the length of time and nature of the alteration process which converts the bulk of the vitreous ash to clay minerals.

This study set out to investigate the time relations of various bentonite constituents by Rb-Sr isochron dating with a view toward possibly confirming K-Ar dating of relatively unaltered materials and attempting to throw some light on the time, duration and nature of the major chemical transformations of the original pyroclastic material.

Bentonite sample

Location: The bentonite used in this study occurs and outcrops at Kinnekulle, Sweden. The bentonite layers of various thicknesses – from an inch up to about six feet- are interbedded with fossiliferous Middle Ordovician limestones and shales. The Cambrian beds at Kinnekulle consist of flat lying sandstone and shale deposited over the Precambrian basement. A post Silurian diabase sill occurs about 100 metres above the bentonite beds. The sill did not metamorphose the bentonites since the "B" horizon is still a swelling, montmorillonite-rich clay (Byström-Asklund, et al, 1961).

A West-East profile of Kinnekulle bentonite (from Råbäcks harbour to Gössäters railway station) is illustrated in figure 1. The sample used for the purpose of dating

in this study was collected from horizon A_1 of the bentonite beds (fig. 2).

Mineralogic-petrographic description: The natural dry Kinnekulle bentonite is a loose, light grey mass with visible flaky brown biotite. Macroscopically, biotite and clay are the only two distinguishable minerals in the bentonite. With more detailed work, the bentonite is found to comprise mainly mixed layer illite and montmorillonite; a little kaolinized plagioclase, biotite, sanidine, quartz; and minor zircon and apatite. Some garnet and pyrite are also observed. No usual detrital materials were found.

From horizon A_1 of the bentonite, the weight percentage of different minerals are estimated: biotite 2-3 per cent, sanidine 0.05 per cent, zircon 0.02 per cent, plagioclase 0.3 per cent, quartz 0.4 per cent and the clay material 90 per cent (maximum).

Biotite often shows idiomorphic grains of euhedral form. Strong pleochroism, high double refraction and a small axial angle ($2V < 10°$) are observed. Chlorite is present and classified as an intermediate between amesite and daphnite (Byström, 1956). The weathering effect on the biotite varies not only from one bentonite bed to another but even from layer to layer within a thick bed. Perhaps due to this uneven weathering effect, the specific gravity of the biotite is found to cover a wide range (from 2.7 to over 3).

Sanidine is completely unaltered. It is a clear, colorless mineral with a specific gravity of 2.57. A composition of 75.2% (by weight) of $KAlSi_3O_8$ and 24.8% of $NaAlSi_3O_8$ (or expressed in molecular composition of $Or_{74}A_{26}$) is given to the sanidine in the thick bed (Byström, 1956).

The ratio of illite to montmorillonite is approximately 2 : 3 for the clay material in horizon A_1. The clay contains layers with intermediate expansion of 14 Å. This fact can be explained by the influence of the higher potassium content, which gives rise to a greater amount of non-swelling layers.

PROFILE OF KINNEKULLE
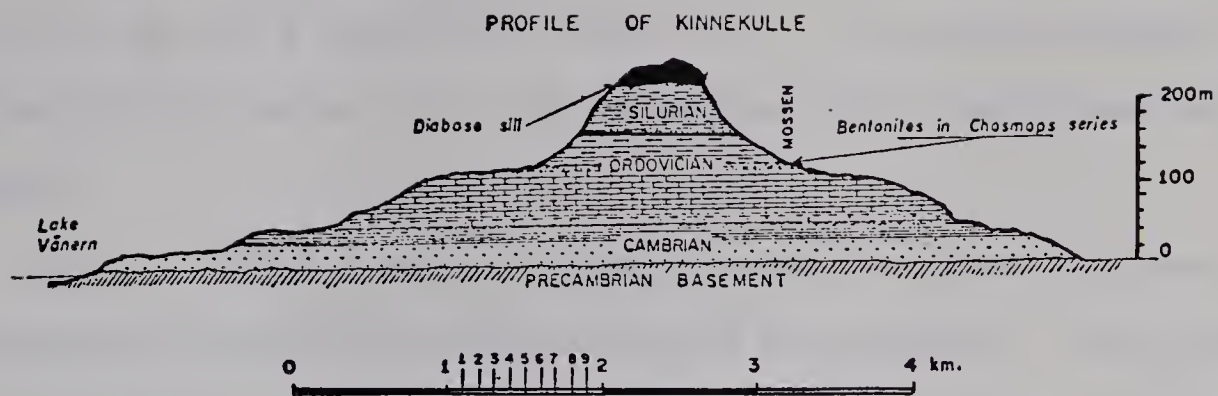
Fig. 1. West-east profile of Kinnekulle from Råbäcks harbor to Gössäters railway station, showing location of Mossen adit (after Westergård, 1943).

SECTION AT MOSSEN, KINNEKULLE
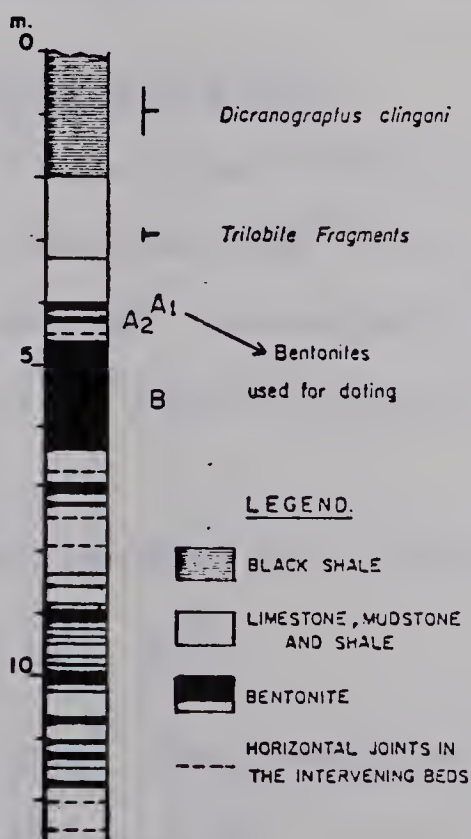
Fig. 2. Bentonite beds in Chasmops series at Mossen, Kinnekulle (after Thorslund, 1948).

Plagioclase has altered to kaolin and quartz. The altered grains are obtained from a fraction with a specific gravity about 2.54. These grains are opaque, or dotted with a light rusty-yellow color. They are soft and readily crushed under the slightest pressure.

Bystrom (1956) believed that weathering process, the cause of alteration of plagioclase, had taken place long after the devitrification of the volcanic ash. The parent magma of the thick beds, according to Byström (1956), could have had a composition corresponding to a rhyolite, or more probably, a dacite. However, the composition of original material that gave rise to the thin beds (including the A_1 horizon) remains unknown.

K-Ar data: The K-Ar age of biotite, sanidine and illite from Kinnekulle bentonite was determined by Byström-Asklund, et al. (1961). They obtained the average date (only from the biotite and sanidine samples) of 444 million years for the bentonite. This is interpretable as the date of deposition of the bentonite.

Mode of experimental approach to the problem

The Rb-Sr method is based on the transformation of Rb^{87} into Sr^{87} by β-particle decay. If Rb_p^{87} is the number of Rb^{87} atoms in a phase at the present time, and λ is the decay constant of Rb^{87}, the relation $Rb_o^{87} = Rb_p^{87} \cdot e^{\lambda t}$ is known, where Rb_o^{87} is the initial number of Rb^{87} atoms in the phase and t is the time elapsed since formation of the phase.

For a rock or mineral considered to be a closed system:

$$Rb_o^{87} - Rb_p^{87} = Sr_p^{87*}$$

where Sr^{87*} is the number of Sr^{87} atoms formed by radioactive decay, and:

$$Rb_p^{87}(e^{\lambda t} - 1) = Sr_p^{87*}$$

together with

$$Sr_p^{87} = Sr_o^{87} + Sr_p^{87*}$$

By substitution:

$$Sr^{87}_p = Sr^{87}_o + Rb^{87}_p (e^{\lambda t} - 1)$$

Using the approximation $(e^{\lambda t} - 1) \approx \lambda t$ when λ is small and dividing both sides of the above equation by Sr^{86} (invariant), the following equation is obtained:

$$\left(\frac{Sr^{87}}{Sr^{86}}\right)_p = \left(\frac{Sr^{87}}{Sr^{86}}\right)_o + \left(\frac{Rb^{87}}{Sr^{86}}\right)_p \lambda t$$

This is the equation of a straight line of the form $y = ax + b$, where $y = \left(\frac{Sr^{87}}{Sr^{86}}\right)_p$; $x = \left(\frac{Rb^{87}}{Sr^{86}}\right)_p$ and the slope of the line, $a = \lambda t$. $(Sr^{87}/Sr^{86})_o$ is the y intercept b.

The line described by the equation $(Sr^{87}/Sr^{86})_p = (Sr^{87}/Sr^{86})_o + (Rb^{87}/Sr^{86})_p \lambda t$ in a plot of $(Rb^{87}/Sr^{86})_p$ vs $(Sr^{87}/Sr^{86})_p$ is called an isochron. An example of the isochron plot is shown in figure 3.

For two co-existing samples of different Rb contents, the sample with the greater amount will produce more Sr during the same interval of time. Consequently it will lie further along the isochron than the sample with less Rb (e.g. minerals I and II in figure 3). The slope of the isochron is proportional to the time elapsed since the system became closed with respect to Rb and Sr. Thus for a rock that has undergone no metamorphism or alteration since crystallization, the whole rock and mineral plots will fall on an isochron giving the time of crystallization (which is the case in fig. 3). This implies that (i) all samples must have had the same initial Sr^{87}/Sr^{86} ratio, (ii) they must all have the same age (i.e. they were formed at the same time) and (iii) the rock must have acted as a closed system.

These assumptions are often valid for a rock that has crystallized from a magma, but are not always true for metamorphic or sedimentary rocks. Bentonite has undergone transportation from its volcanic source into its depositional environment, the transformation of volcanic ash into clay material and possibly diagenesis and/or weathering. As a consequence, it is not likely that bentonite would have been a closed system.
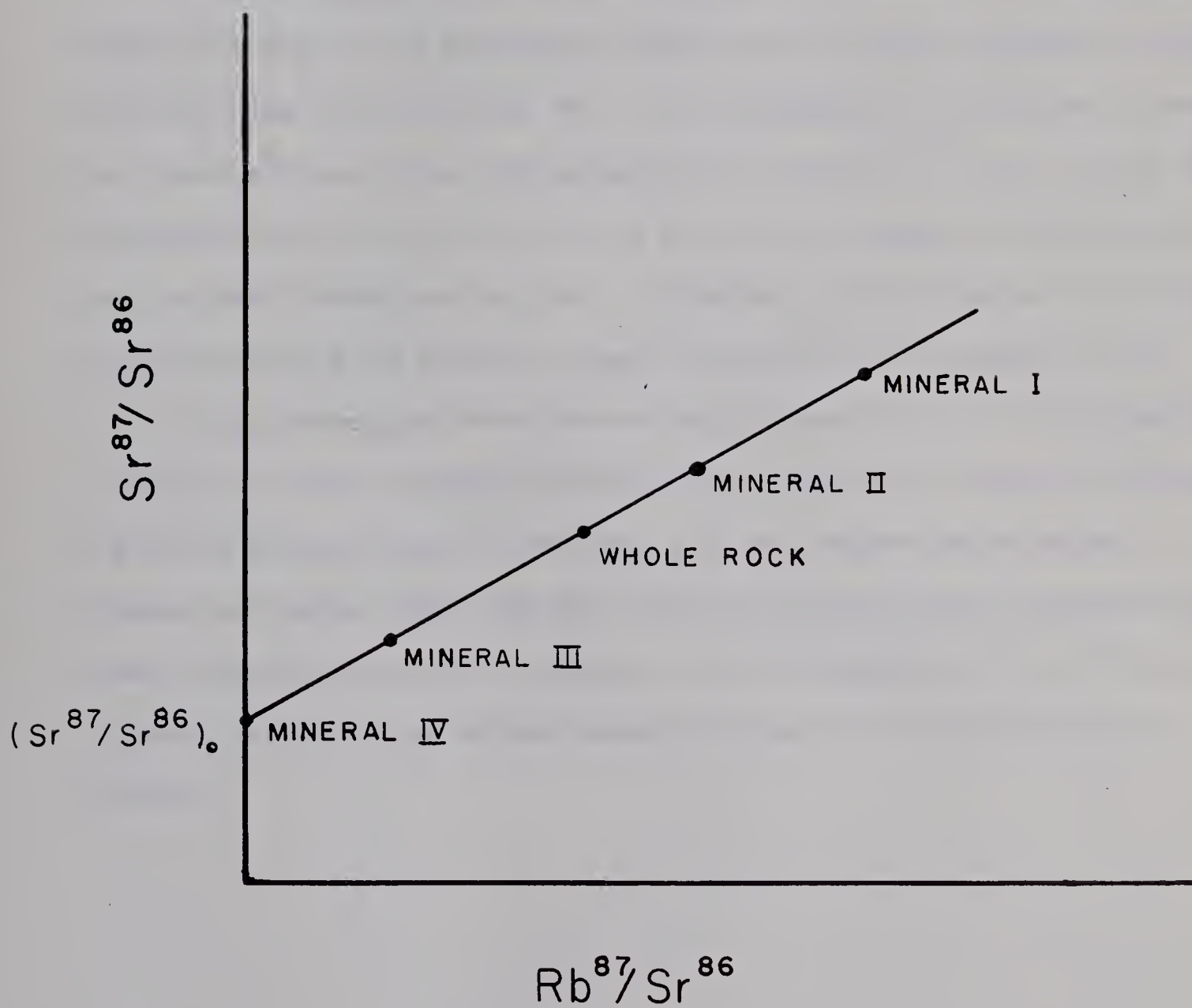
Fig. 3. Whole rock and mineral isochron plot of a closed system.

If by any geological process the bentonite horizon became an open system chemically, a variation in Rb and Sr isotopes as well as in the derived age would be clearly shown in the isochron plot. A deviation of the isochron obtained after the system becomes open from that obtained (or estimated) from unaltered minerals (i.e. minerals with initial compositions) will indicate geochemical variation in Rb and Sr.

When post-depositional Sr loss occurs and Rb is conserved, the slope of the isochron will decrease. A hypothetical initial (unaltered) mineral plotted at A moves to B after Sr loss has occurred (fig. 4a). If only radiogenic Sr is lost and Rb is conserved, the mineral will move along a line perpendicular to the Rb^{87}/Sr^{86} axis, to B (fig. 4b). The date obtained from the mineral now at B is naturally younger than that obtained from the "same" mineral previously at A. When both Sr and Rb are lost, the mineral may move along the line AB and the slope of the isochron also decreases (fig. 4c).

More complex cases where loss and gain of Rb and Sr occur, are quite possible in geological material in general and particularly in bentonite. However, the isochron plot method (alone or together with others, e.g., the Compston-Jeffery method, Compston and Jeffery 1960, 1961) often offers an excellent method to interpret rock and mineral ages and to investigate variations in isotopic compositions of Sr and Rb in an attempt to throw some light on major chemical changes in the bentonite since its formation.
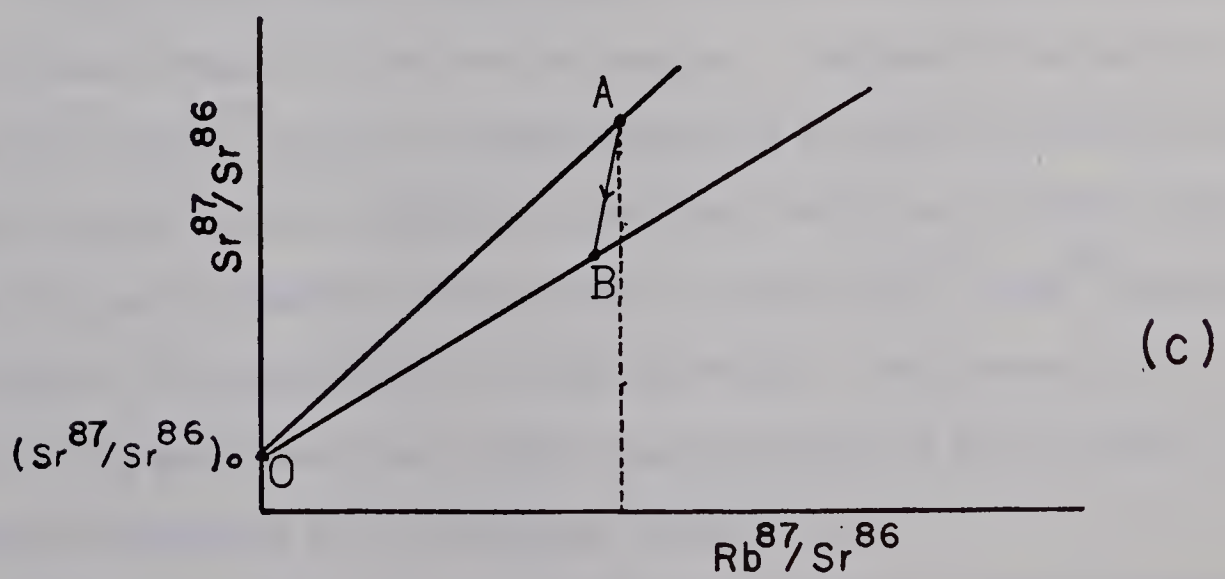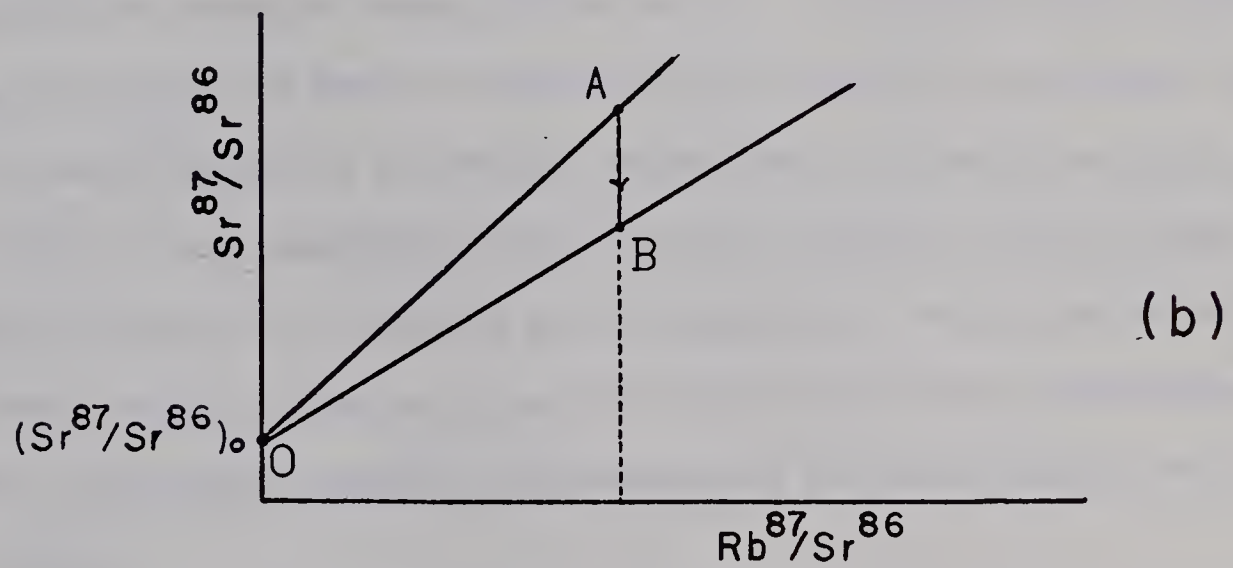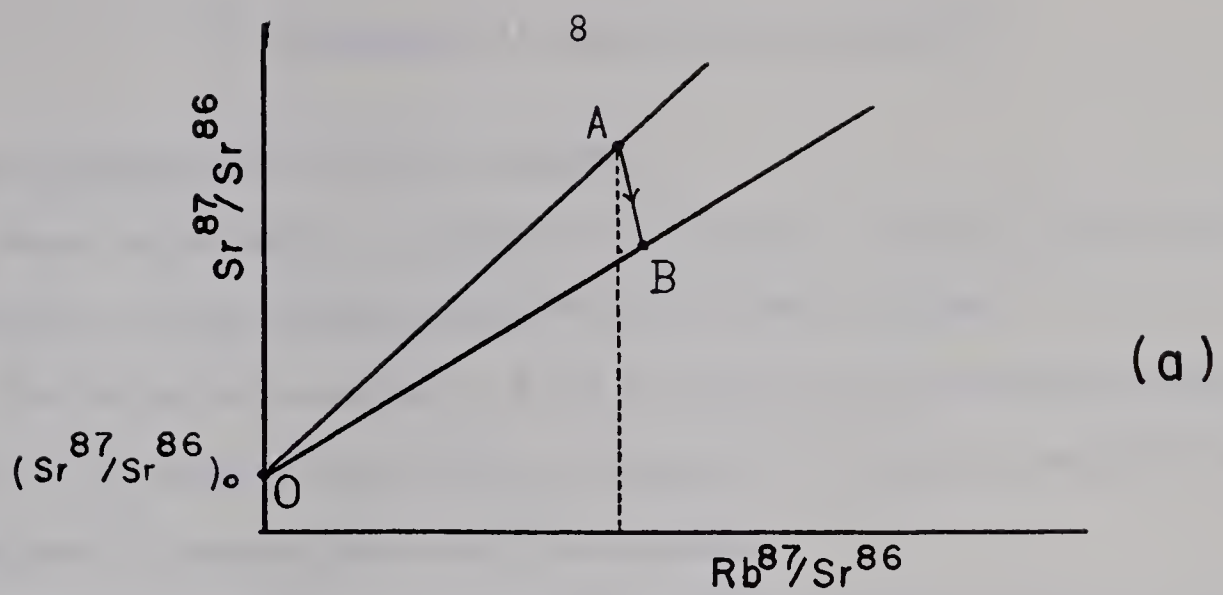
Fig. 4. Changes of a mineral plot in a system with unchanged $(Sr^{87}/Sr^{86})_o$; OA: isochron of true age; OB: isochron of apparent age when

(a) Sr is leached while Rb is conserved
(b) $Sr_{rad.}$ is leached while Rb is conserved
(c) Both Sr and Rb are leached (Sr loss > Rb loss).

II - EXPERIMENTAL PROCEDURE AND RESULTS

<u>Outline of procedure</u> (for details see appendix)

About twenty samples, including the "whole rock", sanidine, biotite and clay minerals were used for age determination by the Rb-Sr method.

The biotites were subjected to X-ray fluorescence spectrochemical analysis for K_2O, Fe_2O_3 (as total Fe) and TiO_2 (see Appendix 1) in order to establish chemical and geochemical relationships between these samples.

In the Rb-Sr method, measurements of daughter and parent elements are best determined by the method of isotope dilution analysis. An accurately known quantity of tracer consisting of the element having an isotopic composition very different from that of the natural element in the sample, is mixed with a solution of the sample. The element (Rb or Sr) to be determined is then chemically separated, and the isotopic composition of the mixture is measured by mass spectrometry. As the isotopic composition of the tracer, that of the mixture (tracer with sample) and the amount of the tracer are known, the isotopic composition and the amount of the wanted element can be easily obtained.

In a mass spectrometer, rubidium ions are produced with greater ease and at a lower filament temperature than those of strontium. The isobaric interference between Rb^{87} and Sr^{87} requires a complete removal of rubidium from strontium when measuring strontium isotopes, especially in unspiked samples (pure samples, without addition of tracer). Therefore, an inaccurate correction of Sr^{87} for Rb^{87} present in a strontium run is a source of error in strontium analysis. The presence of Sr in Rb analysis, on the other hand, has no effect since the emission of Rb ions is about 1.2 - 1.3 amperes compared to 2.3 - 2.5 amperes for strontium.

When determining the isotopic composition of common strontium, the measured Sr^{87}/Sr^{86} ratio is corrected by use of the Sr^{86}/Sr^{88} ratio (0.1194, Nier, 1950) and half of the difference between the true and measured Sr^{86}/Sr^{88} is used to correct

the measured Sr^{87}/Sr^{86} ratio.

The total strontium, radiogenic Sr and Rb are then calculated from the basic isotope dilution equation. The age of a sample is obtained according to t = (% radiogenic Sr^{87}) / (% Rb^{87}.λ). (See Hamilton, 1965, page 81 for derivation). The decay constant λ used in this study is 1.47×10^{-11} yr.$^{-1}$ (Flynn and Glendenin, 1959).

Results

The results obtained by isotope dilution and X-ray analyses are tabulated in Tables 1 and 2.

Reliability of results

The reliability of results is related to the analytical procedure. Variations outside of the precision of the results are taken to be due to geologic factors. Principal error sources are:

    (1) inhomogeneity of the samples

    (2) variable blank contamination

    (3) low content of radiogenic strontium

    (4) imprecise isotopic measurements

(1) Inhomogeneity of the samples: With the procedure of first bringing the sample into solution and then dividing into smaller proportions for the purpose of mixing with Sr and Rb tracers separately (see Appendix 3), the possible inhomogeneity of the sample would not effect the final results. On the other hand, if different amounts of the sample are weighed separately for Sr spiked and Sr unspiked, and the isotopic ratios measured accordingly, the inhomogeneity of the sample could give rise to discrepancy among the measured Sr^{87}/Sr^{86} ratios. This error is reduced by grinding the entire sample to a fine powder.

(2) Variable blank contamination.

Table 1.   Analytical data and age results for Kinnekulle A$_1$ Bentonite, Kinnekulle, Sweden

Sample No.	Mineral	Rb^{87}, ppm	Radiogenic Sr, ppm	Common Sr ppm	Sr^{87}/Sr^{86} atomic ratio	Rb^{87}/Sr^{86} atomic ratio	Rb/Sr age m.y.
N-1-1	Biotite	121.2	0.737	28.6	0.975	43.3	412 ± 12
N-1-2	(45–80 mesh)	114.7	0.684	33.0	0.923	35.5	404 ± 12
N-1-3		80.1	0.368	60.6	0.774	11.1	379 ± 9
N-2-1	Biotite	123.2 (2)	0.709	30.0	0.953	41.9	390 ± 3
N-2-2	(80–170 mesh)	117.6 (2)	0.668	29.6	0.942	40.6	385 ± 6
N-2-3		115.9	0.638	34.8	0.898	34.0	372 ± 6
N-2-4		66.8 (2)	0.387	64.8	0.773	10.5	394 ± 12
N-3	Biotite	121.7 (2)	0.547	19.1	0.995	65.0	305 ± 6
N-3-2	(< 170 mesh)	124.2 (2)	0.607	39.5	0.869	32.1	332 ± 12
N-3-6		57.1	0.341	77.3	0.757	7.5	405 ± 21
N-4-1		46.2	0.210	35.9	0.771	13.1	308 ± 20
N-4-2		45.1	0.202	36.6	0.768	12.1	318 ± 18
N-4-3	Clay	48.9	0.217	50.3	0.756	9.9	302 ± 19
N-4-4		47.9	0.159	42.1	0.750	11.6	225 ± 12
N-4-5		43.4	0.203	52.3	0.751	8.5	317 ± 6
N-11	Sanidine	63.9 (5)	0.445	557.8	0.720	1.2	473 ± 32
N-12	whole rock	47.6 (2)	0.223	27.2	0.795	17.7	321 ± 12

Note: The number in brackets indicates the number of analysis

$$\lambda = 1.47 \times 10^{-11} \text{ yr}^{-1}$$

Table 2. K_2O, Fe_2O_3 (as total Fe) and TiO_2 contents of biotite samples.

	Characteristics of biotite samples	Sample No.	K_2O* per cent	Fe_2O_3* (as total Fe) per cent	TiO_2* per cent	Rb** ppm	K/Rb
45–80 mesh size	heaviest density	N-1-1	7.5	23.6	5.5	427.7	145
		N-1-2	7.0	23.3	5.1	404.9	143
	lightest density	N-1-3	4.1	25.3	3.3	232.6	146
80–170 mesh size	heaviest density	N-2-1	7.5	24.8	5.4	434.8	143
		N-2-2	7.2	23.6	5.3	415.1	144
	lightest density	N-2-4	4.4	25.8	3.4	235.5	155
		N-3	7.2	25.3	5.4	429.6	139
<170 mesh size	heaviest density	N-3-1	7.8	26.2	5.6	460.7	140
		N-3-2	7.4	25.5	5.5	438.4	140
		N-3-3	6.7	25.9	5.5	435.9	127
		N-3-4	6.6	25.2	5.0	293.8	185
		N-3-5	4.6	28.5	3.5	350.4	108
	lightest density	N-3-6	3.6	28.8	2.8	201.5	148

* Determined by X-ray fluorescence
** Determined by isotope dilution

(3) <u>Low content of radiogenic strontium</u>: contamination and error in isotopic measurements contribute most to errors in the true normal strontium content. As radiogenic strontium is calculated by subtracting normal strontium from total strontium, the uncertainty in the normal strontium has a great effect on radiogenic strontium concentration, especially when this concentration is low.

If X represents the amount of radiogenic Sr^{87} and Y, the abundance of normal Sr^{87}; this effect is given by $(\delta X/X)/(\delta Y/Y)$. The variance is expressed as the differential

$$(\delta X/X)/(\delta Y/Y) = - (A/X)Y$$

where A is the amount of normal strontium (Gast, Kulp and Long, 1958). It is also observed that one per cent error in isotopic abundance of Sr^{87} will only result in one per cent error in radiogenic concentration when the ratio of normal to radiogenic Sr is equal to 14. In the present analysis, this ratio is found to be greater than 14 for all biotite samples. However, the measurement error in normal Sr^{87} determination is smaller than 0.5 per cent.

(4) <u>Imprecise isotopic measurements</u>: a major source of possible analytical errors occurs during this operation. The correct choice of the ratio of the sample to the tracer in the mixture has a great effect on the accuracy of the determination of isotopic ratios. With a tracer enriched in Sr^{86} and Sr^{84}, the favorable ratio of measured Sr^{88}/Sr^{86} is usually greater than 2. If $(Sr^{88}/Sr^{86}) \approx 2$, samples with radiogenic Sr content from 13%-5%* tend to give (Sr^{87}/Sr^{86}) around 0.2. The $(Sr^{88}/Sr^{86})_{meas.}$ and $(Sr^{87}/Sr^{86})_{meas.}$ ratios are observed to vary in the same direction (as the result of mixing with tracer). Thus if the $(Sr^{88}/Sr^{86})_{meas.}$ is smaller than 2, then $(Sr^{87}/Sr^{86})_{meas.}$ is less than 0.2. The results corresponding to $(Sr^{87}/Sr^{86})_{meas.}$ of appreciably smaller than 0.2 have relatively low precision.

For most of the samples, the ratios $(Sr^{87}/Sr^{86})_{meas.}$ have typically a standard

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* The radiogenic Sr^{87} percentage is calculated as: $[(Sr^{87}_{rad}) / (Sr^{87}_{rad} + Sr^{87}_{N})] \cdot 100$

deviation of about one part per one thousand. The radiogenic Sr^{87} content calculated

from this $(Sr^{87}/Sr^{86})_{meas.}$ will have an error of the order of 0.5%, provided the sample

contains more than one per cent radiogenic Sr. With a typical standard deviation of

1.5 part per thousand for $(Rb^{87}/Rb^{85})_{meas.}$, the calculated Rb^{87} content will have an

error of .32%, when the sample contains about 50 ppm of Rb^{87}. Thus correspond-

ingly, the error in the age of the sample will be $\lessgtr 1\%$. With all possible errors taken

into account, the total error is estimated to be 3% as a maximum.

However, an exceptionally high error occurs in the case of sanidine owing to

its low radiogenic Sr^{87} content (1.13%*). From analytical data, the results obtained

are as follows:

- radiogenic Sr^{87} in ppm = 0.445 $\pm$ 0.0297 and the corresponding age is 473

  $\pm$ 32 m.y.

- the error in Rb measurement is found to be less than 0.32%.

Thus the error in radiogenic Sr^{87} content and in age determinations of the sanidine is

7%. This is considered a big error and the result should not be taken seriously.

However, it is interesting to note that the lower limit of the sanidine age of 441 m.y.

is not far from that obtained by Byström-Aklund, et al. (1961).

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* The radiogenic Sr^{87} percentage is calculated as: $[(Sr^{87}_{rad})/(Sr^{87}_{rad} + Sr^{87}_{N})]$. 100

III - INTERPRETATION

Nature of chemical alteration

If the mineral assemblage of the bentonite is considered together with chemical analyses of the biotite, probable chemical alterations which have taken place since the formation of the bentonite can be deduced.

Clay formation - Clay represents altered original material and is formed primarily from the decomposition of glass and minerals. As biotite and sanidine are believed to have formed originally in the source of the volcanic ash, only the clay is of secondary origin. The process of the formation of montmorillonite (the predominant clay mineral in the Kinnekulle bentonite) is essentially the devitrification of the natural glass of the ash followed by crystallization of the montmorillonite. In most cases, the ash contains an excess of silica and alkalies compared with its final bentonitic product. An indic- ation of the initial environment containing an excess of silica is the occurrence of a chert bed which underlies the bentonite layers at Kinnekulle.

According to Millot (1942) a mineral of high silica-to-alumina ratio, e.g. montmorillonite, is a stable form in an environment of high cation concentration. Under these conditions, available silica would be high because of the flocculation of the alumina. Thus, it likely appears that the environment of formation of montmorillonite was one of high cation concentration. Alkaline water and the availability of ions of magnesium, calcium and iron are usually cited as conditions necessary for the formation of montmor- illonite (Keller, 1957).

Illite was also identified in the Kinnekulle bentonite. The presence of K^+, Mg^{+2}, Ca^{+2}, and Fe^{+2} and a non-acid environment (but not necessarily stagnant water) have been suggested as conditions favouring the formation of illite (Keller, 1956). Many investigators (Caillère and Henin, 1948; Volk, 1938; Aleshin, 1948; Barshad, 1950; etc.) have found a material with a basal spacing similar to illite was produced from montmorillonite when all the material was throroughly dried at about 110°C.

Thus it is likely that Kinnekulle bentonite was formed under somewhat alkaline conditions with Ca^{+2}, Mg^{+2}, Fe^{+2} and K^{+} ions in solution in concentrations sufficient to affect appropriate cation exchange (Keller, 1957). Montmorillonite was subsequently converted to illite.

Alteration of plagioclase - Plagioclase has altered to kaolin and quartz. The kaolin grains are opaque, colorless or dotted with a light rusty-yellow color.

Alteration of biotite - Wet chemical and X-ray analyses reveal that the potassium content in most of the Kinnekulle biotite is lower than that of normal fresh biotite. This clearly indicates that the biotite has suffered alteration and probably is somewhat weathered. According to Walker (1949) the first stage of weathering of biotite involves replacement of potassium ions by water molecules, forming hydrobiotite. Ferrous iron is oxidized, (OH^{-}) replaces O^{-2} and Mg^{+2} is lost, but the flakes remain physically stable. It appears that the same process has affected the Kinnekulle biotite. The alteration process was probably not very extensive because the biotite preserves a small 2V and high birefringence.

As a consequence of weathering, potassium is extracted from the structure of biotite. Having a well marked similarity in geochemical behaviour, Rb is expected to behave in a similar manner. Figures 5a, 5b and 5c illustrate the relationship between K and Rb in the biotites. Biotites were separated on the basis of specific gravity. Potassium contents were determined by X-ray fluorescence and rubidium, by isotope dilution.

A close relationship between potassium and rubidium contents is clearly shown (fig. 5a, 5b and 5c). A trend of decreasing Rb and K is observed passing from heavier biotites to lighter ones within those of the same size range.

Weathering of biotite causes a decrease in density. The more weathered a biotite is, the lighter it becomes and the more K and Rb are leached. This explains
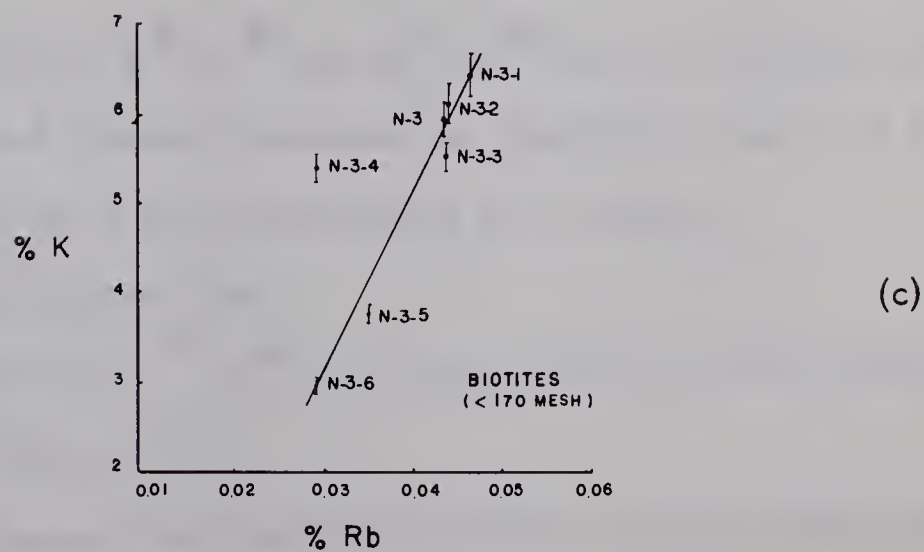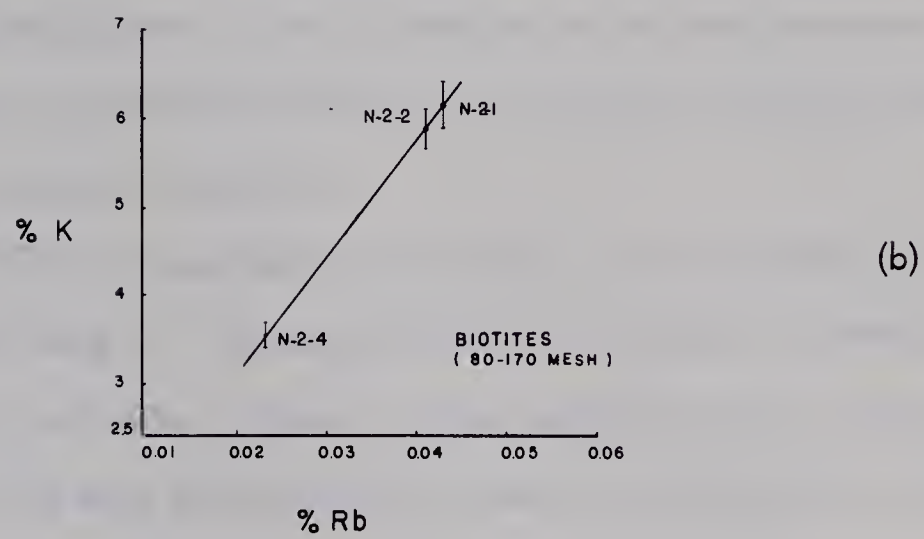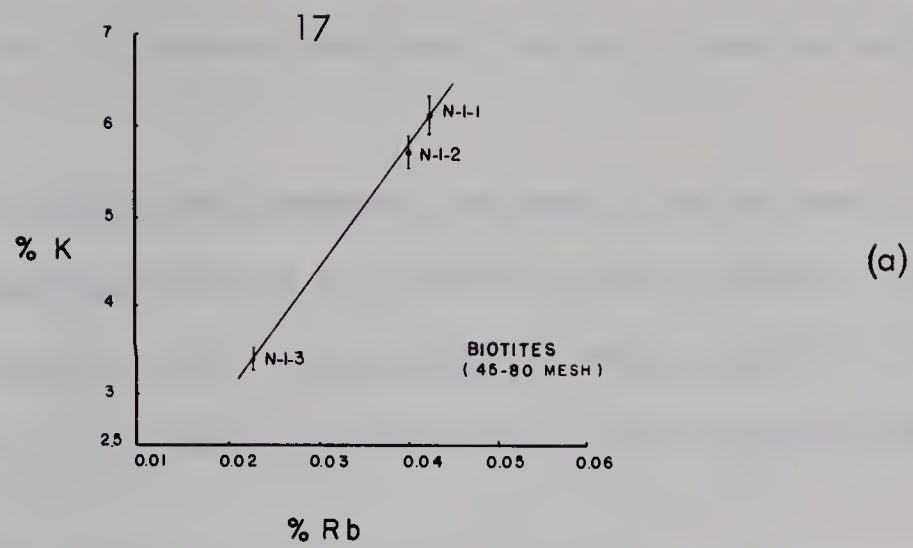
Fig. 5. Potassium and Rubidium relationship in biotite samples.

the relatively low Rb and K contents of the lighter biotites as compared to those of heavier ones.

It is found that Ti content also decreases consistently from the heavy to lighter biotites (Table 2). The role of titanium in the biotite structure remains in some aspects uncertain. It substitutes mainly in octahedral sites but diadochic substitution of titanium for silicon in the silicon-oxygen tetrahedra is also suggested (Rankama and Sahama, 1950).

Characteristically, biotite alters to chlorite, often with the release of titanium to form leucoxene or tiny crystals of rutile (Moorhouse, 1959). The outer part of some Kinnekulle biotites appears to alter to chlorite, but neither leucoxene nor rutile is observed. Probably Ti released from the biotite in this case is entirely leached and does not form any secondary Ti-minerals.

While K, Rb and Ti are leached from the biotite, its iron content remains substantially unchanged (Table 2). No separate analysis was made to determine Fe^{+2} and Fe^{+3} contents in the biotites. However, when weathering occurs, ferrous iron is oxidized. Thus in the more altered biotite probably most of the iron is in the form of Fe^{+3}.

Geochronology

The individual ages, Sr^{87}/Sr^{86} and Rb^{87}/Sr^{86} ratios of minerals and the "whole rock" sample of Kinnekulle bentonite are illustrated in Fig. 6. A meaningful isochron is not drawn due to the wide scattering of the samples.

From Fig. 6 one observes that:

(1) All samples have Sr^{87}/Sr^{86} ratios ranging from 0.712 to 1.004 and Rb^{87}/Sr^{86} from 0.7197 to 0.9750.

(2) The clays group closely between the "whole rock" plot and the initial ratio (0.712) given by apatite.

(3) The "whole rock" has an age of 321 ± 12 m.y. which is lower than that
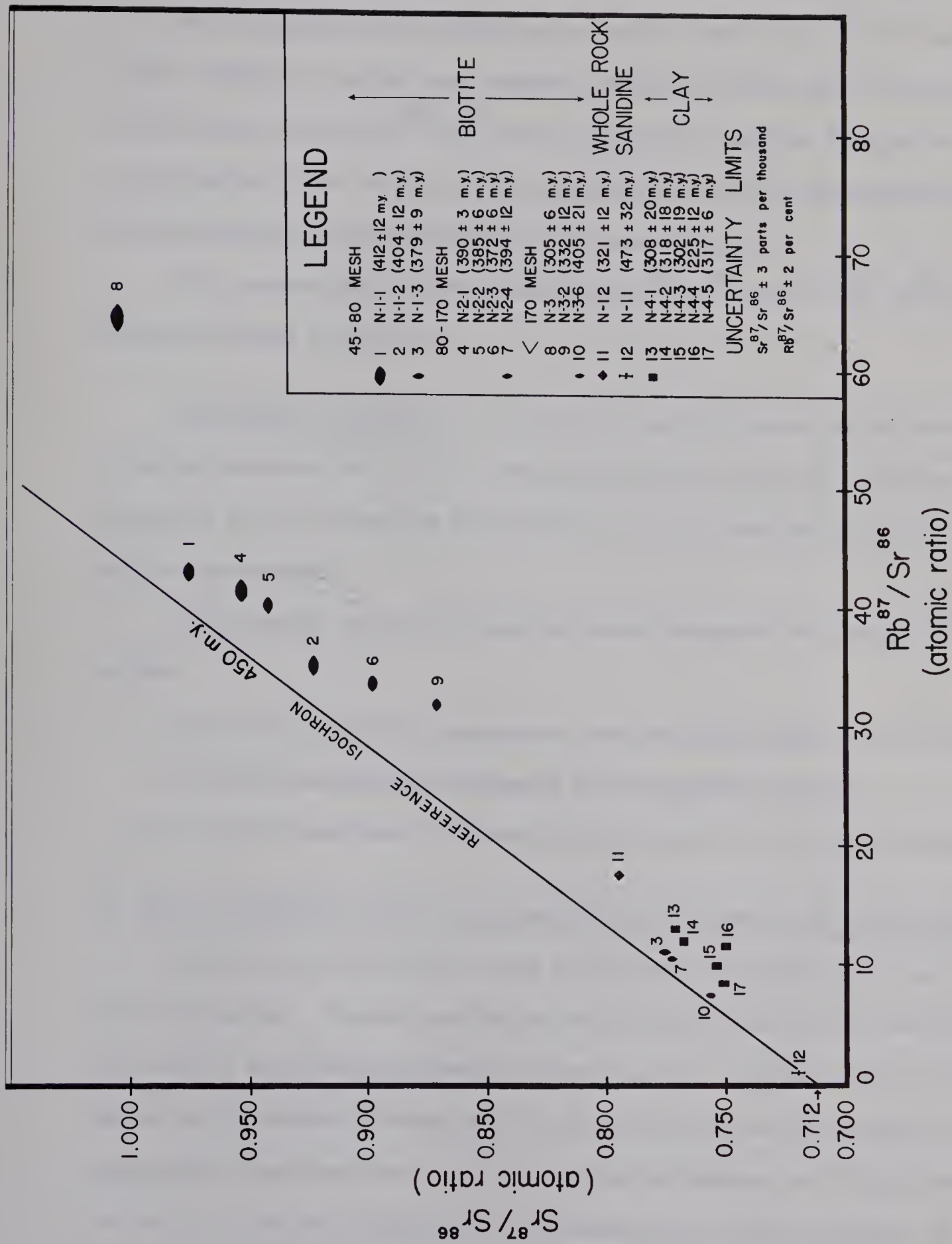
Fig. 6 Isochron plot of minerals from the Kinnekulle A₁ bentonite.

of the biotites.

(4) The biotites form a pattern with a wide variation in Sr^{87}/Sr^{86} and Rb^{87}/Sr^{86} values. Biotites of smaller size (especially samples with high specific gravity) tend to deviate further from the Sr^{87}/Sr^{86} axis as compared to biotites of larger size. More-over, biotites of the same size range but different densities* have a tendency to trend both downward and to the left side of the diagram (fig. 6).

(5) Sanidine has low co-ordinates (low Sr^{87}/Sr^{86} and low Rb^{87}/Sr^{86}) but the highest date (473 ± 32 m.y.).

Chronology of alteration - In section III- (page 15) some possible post-depositional alteration processes taking place in the bentonite were mentioned. Weathering and diagenesis and their effects on the bentonite as a whole and particularly on the biotite will now be discussed.

Three possible sequences of weathering and diagenesis could occur with regard to time.

(i) Initial 'weathering' process at or near the time of deposition of the bentonite.

(ii) Initial 'weathering' followed by slow diagenetic alteration.

(iii) Initial 'weathering' followed by slow diagenesis and recent weathering.

(i) Initial 'weathering' process at or near the time of deposition of the bentonite.

The glassy volcanic ash (by virtue of cryptocrystalline nature) was very suscep-tible to alteration. The ash would be out of equilibrium with the new environment into which it was transported from the volcanic source. In direct contact with sea water, the chemical alteration of the ash could easily take place during or immediately after deposition. Thus, in a marine environment with a high concen-tration of calcium and magnesium ions, montmorillonite could be formed. As

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* Samples having the same letter and the first number belong to the same mesh size range. The larger the second number, the lighter is the sample. Ex: N-1-1, N-1-2, N-1-3 are the samples in order of decreasing density of 45-80 mesh.

previously mentioned, the alteration of the volcanic ash to form montmorillonite involves the significant addition of H_2O and Mg^{+2} ions (Keller, 1957). The alteration process likely began with hydrolysis accompanied by hydration. Silica and alkalies were first removed. Under these chemical conditions, biotite was undoubtedly somewhat affected. Together with K^+ and Ca^{+2}, Rb and Sr were partly removed from the biotite. Subsequently the biotite gained radiogenic Sr until present time. Thus, if the duration of the initial 'weathering' was of the order of one million years, this chemical alteration in biotite would negligibly affect the time relation observed in an isochron plot (because the Sr^{87}/Sr^{86} and Rb^{87}/Sr^{86} ratios would remain essentially the same regardless how Rb and normal Sr might have changed). Consequently, the date given by the biotite would indicate the time of deposition of the bentonite. Obviously, this supposes that the biotite did not undergo any other significant chemical alterations besides the initial 'weathering' during which the formation of montmorillonite took place.

(ii) <u>Initial 'weathering' followed by slow diagenetic alteration</u>

It is clear that diagenetic process did occur because the formation of illite resulted from the fixation of K^+ by montmorillonite, and the ash initially was permeable and porous. With the development of clay minerals, especially the hydrated species, pore spaces would be partially filled by the increased volume of material. At the same time, compaction took place under the load of superimposed strata. During compaction, chemical alteration could readily occur, aided by the squeezing out of pore-space fluids.

The effect of the initial 'weathering' on biotite would be the same as in the first case.

<u>Effect of diagenesis on biotite</u>: During compaction, it is likely that hydration was the main chemical reaction with addition of such cations as Ca^{+2}, Na^+ and

possibly leaching of others, e.g. K^+. Water molecules replaced K ions in biotite.

As mentioned previously, the isochron of biotite on fig. 6 appears to depend on both their sizes and their densities. This fact makes it necessary to consider the effect of diagenesis on the size and density of the biotite.

Density effect: The biotite is partly altered to chlorite. Suppose that the alteration is not evenly distributed among the biotites. Samples in direct contact and for a longer time with sea water (or water in the confining strata) would be more altered than those with little contact with the water. As the result, we could expect that for samples which are more altered (a) their density would be lower than that of less altered biotites; (b) K, Rb and radiogenic Sr were leached more easily and to a greater extent than in less altered biotites. This is observed to be true since biotites of the same size range show a decrease in K, Rb and radiogenic Sr contents with a decrease in density (Table 3, columns 1, 2, 3). It is possible that Rb^{87} and radiogenic Sr^{87} were both leached to the same extent. This is a reasonable hypothesis as radiogenic Sr^{87} is derived from Rb^{87} (by β decay) and is located in the same site as Rb^{87} in the lattice.

One definite observation is that normal Sr increases from the heavy to lighter biotites (Table 3, column 4). This seems to indicate that biotites undergoing alteration (probably chloritization) gained normal Sr. Biotites in contact with Sr-bearing solution for a longer time (i.e. more altered) would gain more normal Sr. The supply of Sr could come from other altered components of the bentonite (e.g. plagioclase which is rich in Sr and poor in Rb).

Size effect: Biotites of small dimension have relatively higher Rb^{87}/Sr^{86} ratios than those of larger size. This effect may be caused by (i) a gain in Rb or (ii) a higher loss of radiogenic Sr in biotites of smaller size.

To support the first argument, Gerling and Ovchinnikova (1962) experimentally found that partial substitution of K by Rb in biotite was possible in a Rb-bearing

Table 3. Variations in K, Rb and Sr contents of biotite samples of different densities and size ranges.

SAMPLES			K, per cent	Rb, ppm	Sr^{87*}, ppm	Sr^N, ppm
Mesh size	Density	Sample No.				
	heaviest	N-1-1	6.2	121.2	0.737	28.6
45-80		N-1-2	5.8	114.7	0.684	33.0
	lightest	N-1-3	3.39	80.1	0.368	60.6
	heaviest	N-2-1	6.2	123.2	0.709	30.0
		N-2-2	6.0	117.6	0.668	29.6
80-170		N-2-3		115.9	0.636	34.8
	lightest	N-2-4	3.6	66.8	0.387	64.8

solution nearly free from other ions. In the case of the Kinnekulle biotite, Rb enrichment is unlikely to have occurred as K/Rb ratios are almost the same for samples in 45-80 and 80-170 mesh size ranges (Table 2). However, lower K/Rb ratios (Table 2) and the consequent   higher slope of the plot in fig. 5c suggest that a later Rb enrichment might have occurred in biotites of small size (smaller than 170 mesh).

On the other hand, it is apparent that biotites of small dimensions seem to lose their radiogenic Sr more easily than those of larger size. This can be considered as a "volume effect" if the alteration process starts at the outer part and proceeds inwards in the biotite structure. For a comparison, Hurley, et al. (1960) found that metamorphism expelled all ragiogenic argon from finer grain-size muscovite, but larger flakes retained some argon.

(iii) Initial 'weathering' followed by diagenesis and recent weathering

The initial 'weathering' would have the same effect on biotites as discussed in the first case.

As no sharp boundary between diagenesis and weathering can be drawn (Sujkowski, 1958) the difference in chemical alterations which have taken place in diagenesis and in weathering are impossible to define. Thus the recent weathering and its clear effects on the bentonite would be difficult to consider.

Goldich and Gast (1966) have found that weathering has drastically reduced Rb-Sr and, to a lesser extent, the K-Ar age of residual biotite derived from the Morton gneiss of southwestern Minnesota. On the other hand, Millot (1963) has suggested that the alteration of biotite to chlorite could be due to either weathering or diagenesis. If so, the effects of chemical alteration on biotite discussed in the second case (diagenetic alteration) could be applied here.

Models of chemical alteration in biotite

As the Kinnekulle bentonite occurs in the Lower Chasmops series of the

Caradocian (Thorslund, 1948), the bentonite must be older than 435 m.y. (based

on Holmes' time-scale). The true age of the bentonite is assumed to be 450 m.y.

(based on K-Ar data, Table 4 and independent time-scales). The relatively low Rb-Sr

dates of biotite samples ($<$ 424 m.y.) undoubtedly imply that the biotite has suffered

some chemical alteration with a resultant change in isotopic composition. In attempting

to explain these chemical changes, three possible histories or sequences of alteration

processes will now be considered.

(i) <u>Initial 'weathering'</u>: As previously mentioned (see page 20) the initial

'weathering' has no effect on the ultimate time relationships in a plot of Rb^{87}/Sr^{86} vs

Sr^{87}/Sr^{86}, but only on the absolute isotopic abundances in the biotite. Consider the

schematic plot in fig. 7. At $t = 0$ (i.e. 450 m.y. ago) apatite, sanidine and biotite

form an isochron parallel to Rb^{87}/Sr^{86} axis. From $t = 0$ to $t < 1$ m.y. (assumed to be

the duration of the initial 'weathering') changes in the original isotopic composition

of biotite take place, resulting in various biotites with different chemical compositions

(a, b, and c, in fig. 7). Subsequently, (from $t = 1$ m.y. onward) radiogenic strontium

is steadily accumulated without undergoing any loss. Thus Sr^{87}/Sr^{86} increases in the

course of time. At $t = t_p$ (= 450 m.y.) biotites together with sanidine and apatite

(the latter two have not undergone any chemical alteration) form the isochron of 450

m.y. Obviously, the initial 'weathering' is not the process accounting for the low

dates of biotites.

(ii) <u>Initial 'weathering' followed by differential diagenetic alteration</u> (fig. 8):

During the initial 'weathering', the biotite suffers the same chemical changes as

described above up to the time $t \approx 1$ m.y. Then, a diagenetic differential loss of Rb

and Sr occurs between $t \approx 1$ m.y. to $t = t_1$. At $t = t_1$, owing to this differential loss,

the biotites lie along the isochron of a time $t < t_1$, say $t = t_1 - x$, instead of the

isochron of $t = t_1$. Subsequently, as chemical alteration no longer takes place in

the biotites, radiogenic Sr is accumulated without being lost. However, at $t = t_p =$

Table 4. K-Ar Dates of Minerals from Kinnekulle Bentonites (after Byström-Asklund,

et al. 1961).

AK No.	Horizon	K_2O per cent	Ar^{40}/K^{40}	Date, m.y.	Description of Mineral
Biotites (varying degree chloritization)					
82	A_1	5.37	0.0287	434	Almost unaltered flakes.
200	A_1	7.60	0.02594	396*	
77	A_2	4.43	0.0303	453	Coarse, somewhat chloritized.
59	B	3.48	0.0288	434	Strongly chloritized flakes.
Sanidines (varying purity of separation)					
61	B	10.96	0.0304	455	Sanidine (and illitic aggregates).
90	B	11.16	0.0296	445	
146	B	12.08	0.0292	440	Pure sanidine.
Average sanidine date......... 447 ± 20 m.y.					
Illite (whole bentonite, less biotite)					
69	A_1	4.94	0.0213	331	Illitic clay, trace sanidine.

Constants: $\lambda_e = 0.589 \times 10^{-11} yr^{-1}$, $\lambda_\beta = 4.76 \times 10^{-10} yr^{-1}$

K^{40}/K normal $= 0.01181$ atomic per cent

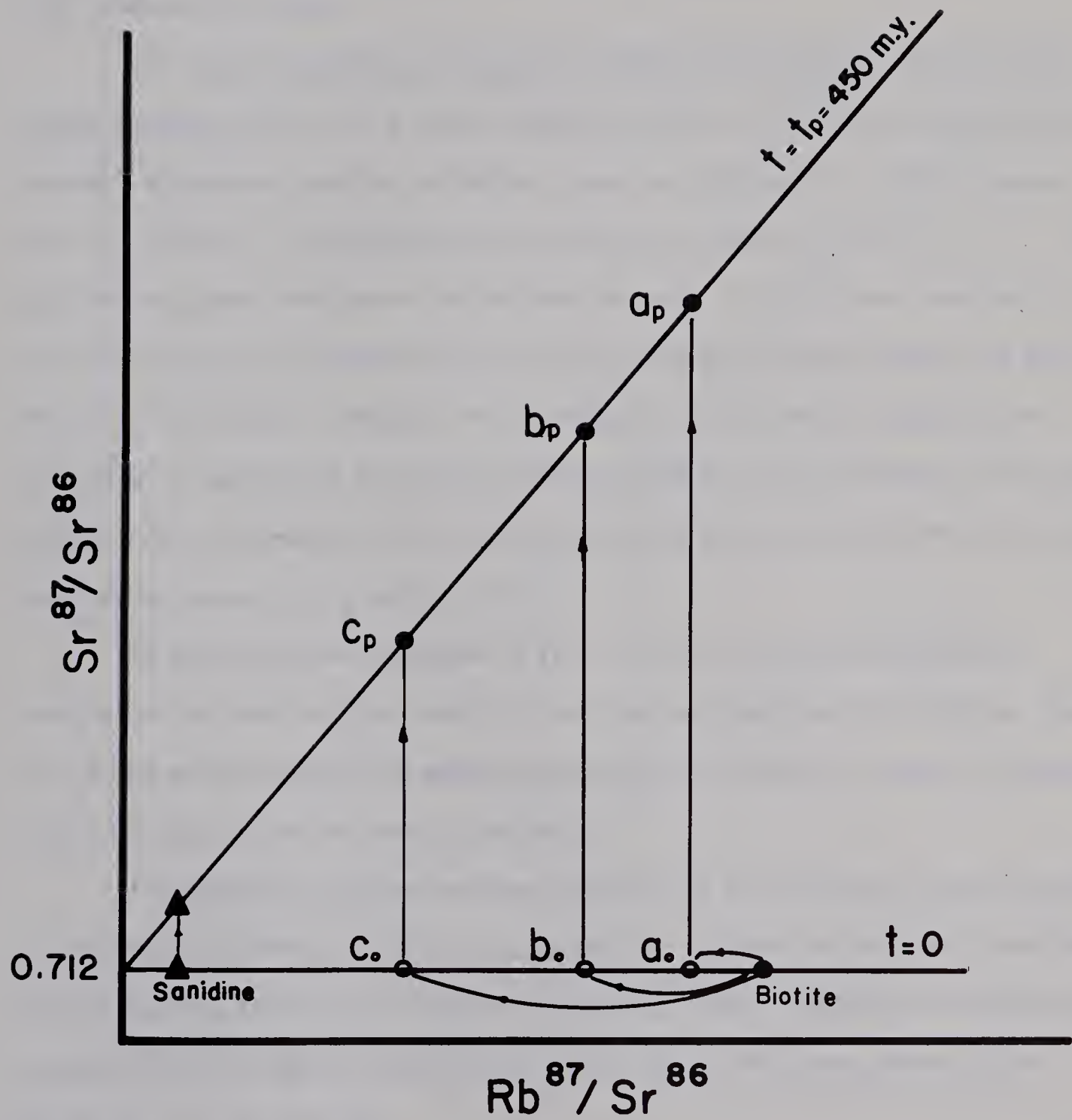*Baadsgaard, H., personal communication.

Fig. 7. Isochron plot formed by sanidine and biotites when only
initial 'weathering' occurs.

450 m.y. the biotites form an isochron of about 410 m.y. instead of 450 m.y. owing to the loss of Rb and Sr taking place from $t \approx 1$ m.y. to t_1. Thus, the dates obtained from biotites are low, while sanidine probably offers a true date as it never underwent chemical alteration.

(iii) <u>Initial 'weathering' followed by differential diagenetic alteration and recent weathering</u> (fig. 9): If recent weathering follows the initial 'weathering' and the early diagenesis, biotites will suffer a great loss in Rb and Sr. For this reason, at $t = t_p = 450$ m.y. the biotites form an isochron of a date $t < t_p$, say $t = t_p - x$. The biotites move down the slope of the isochron at $t = t_p - x$ if the recent weathering in biotites is caused by a simple lattice destruction and approximately equal rate loss of Rb and Sr is involved. However, the 'density effect' (discussed on page 22) and adsorption or leaching of Sr and Rb to different extents can be introduced in the altered lattice. As a consequence, the biotite plots may be widely scattered after the recent weathering occurs (a_p, b_p and c_p in fig. 9).

Of the three cases illustrated in fig. 7, 8 and 9, the last one (fig. 9) is selected as the most probable model for the chemical alteration in the biotite. Thus, it is believed that at least two alteration processes - diagenesis and recent weathering - are responsible for the low date of the biotite.

The hypothesis of recent weathering being one of alteration processes accounting for Rb-Sr up-dating in biotite is supported by considering an example of weathered biotite from the Morton gneiss (Goldich and Gast, 1966). The recent weathering has reduced the Rb-Sr age by approximately 75 per cent of the corresponding age of biotite from the fresh gneiss.

Goldich and Gast (1966) have found their biotite samples lost iron and radiogenic strontium but absorbed rubidium during weathering. On the other hand, the Kinnekulle biotites seem to lose both radiogenic strontium and rubidium while retaining their iron. Different weathering conditions in the two environments could be
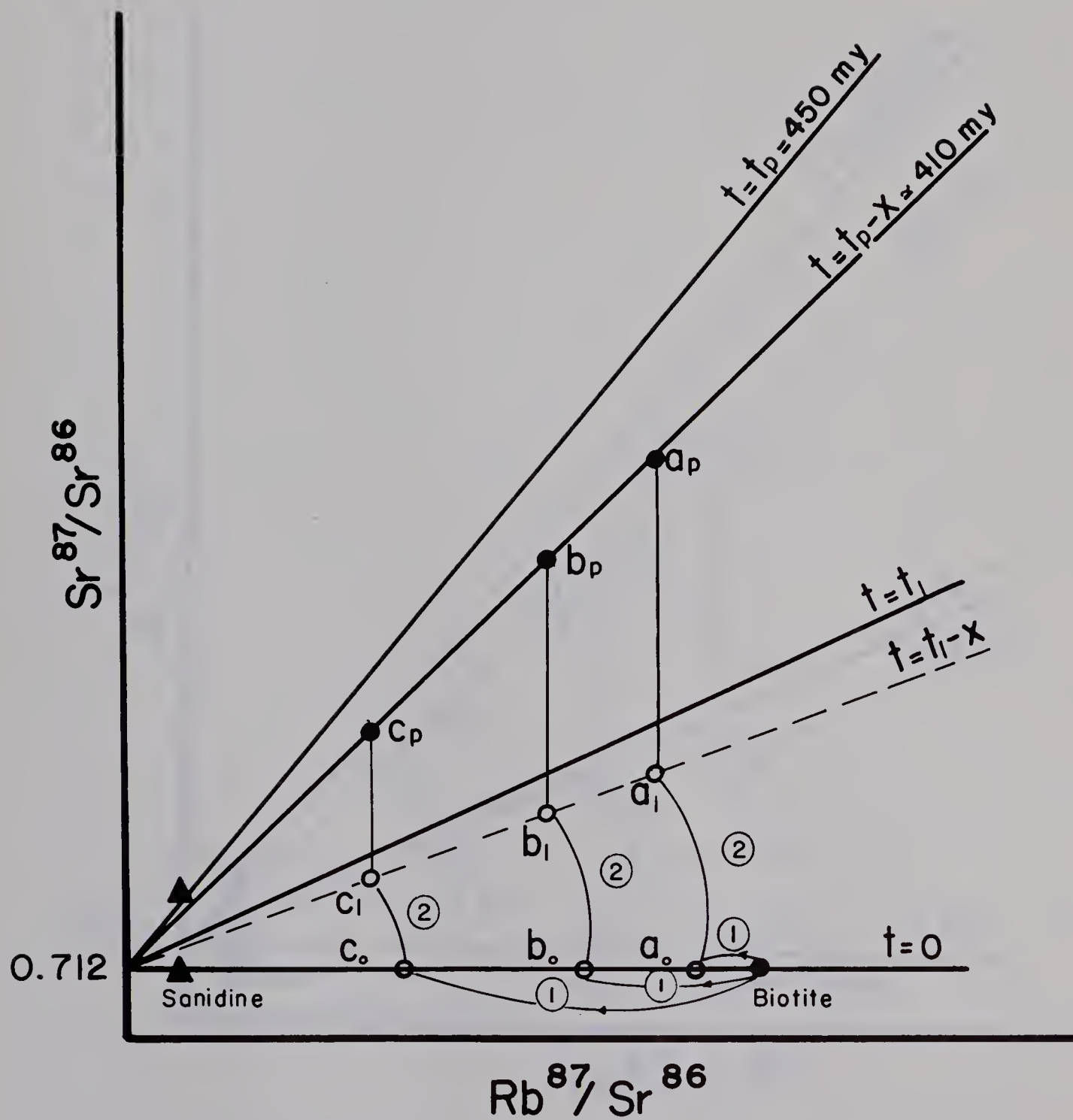
Fig. 8 Isochron plot formed by sanidine and biotites in a
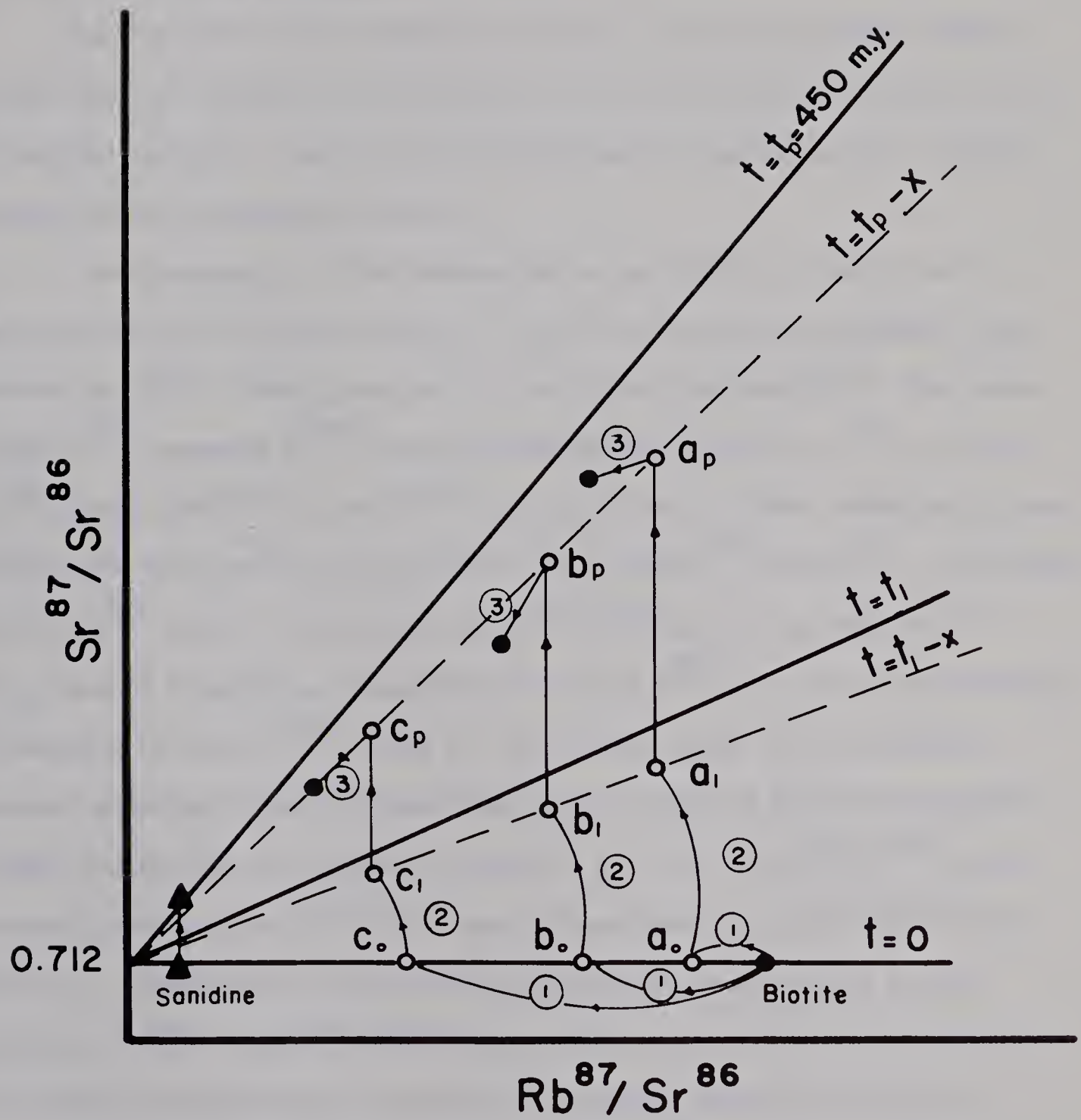sequence of (1) initial 'weathering' and (2) diagenetic
alteration.

Fig. 9. Isochron plot formed by sanidine and biotites in a sequence of (1) initial 'weathering', (2) diagenetic alteration and (3) recent weathering processes.

the cause of differences in the alteration process in the biotite. The occurrence of

rubidium adsorption in biotite likely depends on the availability of Rb ion present

in the solution during weathering.

The 'hypothesis of two alteration processes' is further supported by another

observation from discordant U-Th-Pb dates of zircon from the same horizon A_1 of the

Kinnekulle bentonite. The U-Th-Pb data (Baadsgaard, unpublished data, personal

communication) is tabulated in Table 5.

The discrepancy in U-Th-Pb dates can be explained by a combination of

early uranium loss and recent lead loss. Early in the history of the radiogenic lead

production, Pb^{207} is being produced at a much higher rate than Pb^{206}. The reason

is that U^{235}, parent of Pb^{207}, has a much shorter half life (7.13×10^8 yrs.) than

U^{238}, parent of Pb^{206} ($T^1/_2$ of $U^{238} = 4.51 \times 10^9$ yrs.). If then, subsequent U-loss

substantially decreased the net production rate of both Pb^{207} and Pb^{206}, a net relative

gain of Pb^{207} results. Consequently the Pb^{207}/Pb^{206} ratio is too high, which in

turn, leads to a high date. A possible indication of U^{238} loss is its low concentration

as compared to that of Th^{232} (Table 5). On the other hand, recent weathering

causes a great loss of lead in zircon (Stern, et al. 1966). As Russell and Farquhar

(1960) have pointed out, the effect of lead loss is to lower the Pb^{206}/U^{238} prop-

ortionally more than the Pb^{207}/U^{235} date. The extremely low Pb^{208}/Th^{232} date

(67 m.y.) is probably due to the relatively great effect of lead loss on a small

amount of Pb^{208}. The Pb^{207}/Pb^{206} date is unaffected by lead loss since the date

calculated is based entirely on the relative abundances of the two isotopes (i.e.

their ratio). A greater insensitivity of the Pb^{207}/Pb^{206} date to loss of lead can

be expected when the loss takes place within the last tenth of the life time of the

mineral (Russell and Farquhar, 1960). As a result, the Pb^{207}/Pb^{206} date still

remains high owing to the early U-loss.

Table 5. U–Th–Pb data and isotopic ages of zircon from horizon A_1, Kinnekulle bentonite. (Baadsgaard, unpublished data).

Concentration ppm		Relative abundances		Ages, m.y.
Th^{232}	696.9	Pb^{206}/U^{238}	0.05407	343
U^{235}	3.854	Pb^{207}/U^{235}	0.4292	367
U^{238}	538	Pb^{208}/Th^{232}	0.00325	67
Pb^{206}	25.18	Pb^{207}/Pb^{206}	0.0576	530
Pb^{207}	1.457			
Pb^{208}	2.034			

The presumed effect of early U-loss and recent Pb-loss on the apparent U-Th-Pb dates of zircon from horizon A_1, Kinnekulle bentonite is illustrated in figure 10.
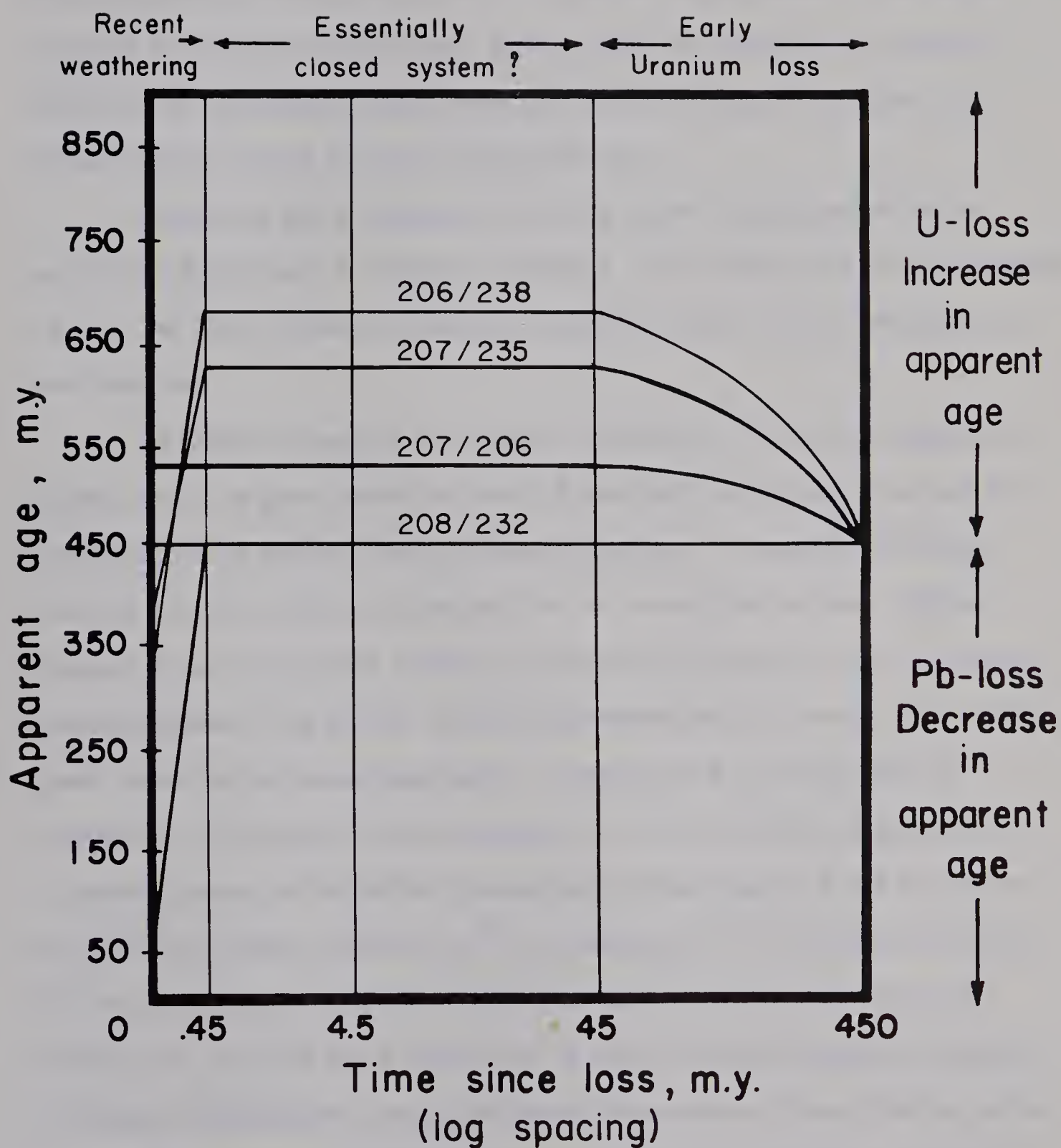
Fig. 10. Presumed effect of early U-loss and recent Pb-loss
on the apparent U-Th-Pb date of zircon from the
Kinnekulle A₁ bentonite. Age of the bentonite is
taken to be 450 m.y.

SUMMARY AND CONCLUSIONS

Various constituents of the Kinnekulle bentonite have been investigated
for their isotopic compositions by the Rb-Sr isochron dating method. The scatter
of points in the isochron plot clearly indicates that the Kinnekulle A_1 bentonite
and all of its constituent (except sanidine and apatite) minerals have been open
systems at some time in the history of the bentonite.

Weathering and/or diagenesis must have had an insignificant effect on
sanidine as this mineral is completely unaltered. The sanidine date (by both methods
of K-Ar and Rb-Sr radiometric dating) is probably nearest to that of deposition of
the bentonite.

Variations in chemical and isotopic composition of the biotite depend to a
certain extent on grain size and on results from alteration processes. Between two
weathered biotite samples having different dimensions, the sample with smaller
size has lost more radiogenic strontium than the one with larger size. Different
degrees of weathering result in different densities of biotites; the lower the density,
the more altered is the biotite. More altered biotite has lost more K, Rb and radio-
genic strontium than less altered biotite. Leaching of K is a direct effect of
weathering. Leaching of Rb and radiogenic Sr is the immediate consequence of
K leaching owing to the similarity in geochemical behaviour of K and Rb, and to
the identity in lattice position of Rb^{87} and radiogenic Sr^{87} in the biotite structure.
On the other hand, a more altered biotite contains more normal Sr than a less
altered one. It is felt that a combination of effects from both diagenetic alteration
and recent weathering has caused the present distribution of altered biotite species.

The discordance in U-Th-Pb dates of zircon is also reasonably explained
by the effects of diagenetic and recent weathering processes. The diagenetic alter-
ation takes place early in the history of the bentonite and causes U-loss, while
recent weathering accounts for the lead loss in zircon.

Weathering of bentonite is readily detected by a mineralogic and petrographic study of plagioclase present in the bentonite. The discordance in ages of minerals in the bentonite suggests that bentonite, once weathered, is unsuitable for dating by the Rb-Sr method. The U-Pb method offers discordant dates as well. However, a combination of the two methods is useful in interpretation of the data. Consequently, an attempt can be made to trace the probable history or sequence of geochemical alteration processes which have taken place in the bentonite in particular, or in any other system in general.

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APPENDIX I

X-RAY FLUORESCENCE ANALYSIS

Analytical method

All X-ray fluorescence analyses were carried out on a Norelco standard X-ray spectrometer equipped with chromium tube. Fe_2O_3 (total Fe) was determined with an LIF analysing crystal, using scintillation counter. TiO_2 and K_2O were determined with EDDT crystal and proportional counter. An evacuated path was used in K_2O determinations.

Tablets for the analysis were prepared from homogenous samples together with borax at 18,000 psi. Table 6 shows the operating conditions.

Calibration procedure and accuracy

Calibration curves were obtained using wet-chemically analysed biotites and muscovite as standards.

Potassium contents of some biotite samples were also determined by a modified Abbey method (Abbey, et al. 1960). When these results were compared with those given by the X-ray fluorescence method, the deviation was found to be less than 5 per cent.

Table 6. Operating conditions for X-ray fluorescence Analysis.

Elements	Crystal	Peak used	Peak location 2θ°	Background 2θ°	X-ray path	Counter	Voltage (volts)
K_2O	EDDT	$K_{\alpha1} + K_{\alpha2}$	20.17	21.40	Vac.	F.P.	1980
TiO_2	EDDT	$K_{\alpha1} + K_{\alpha2}$	6.22	8.50	Air	F.P.	1920
FeO_3	LIF	$K_{\alpha1} + K_{\alpha2}$	57.51	59.00	Air	Scint.	870

APPENDIX 2

MINERAL SEPARATION

First the sample of the whole bentonite in a dry state was put into a large beaker (about 3 inches in diameter) filled with water and thoroughly stirred. It was allowed to settle in order to separate two fractions - 'grit' fraction and clay fraction - from each other. The 'grit' fraction, being heavier, tended to sink quickly. In order to be able to get the minerals reasonably free from the clay and vice versa, the whole sample was first stirred in a blender.

Clay Separation

When the large particles had sunk, the liquid was carefully decanted into another beaker. This liquid, which contained mainly clay, was then stirred, allowed to settle, and decanted into a second beaker. This procedure was repeated several times until essentially only the clay fraction remained. The fine and coarse materials in this clay were concentrated into two fractions by the method of decantation described below:

The procedure involved two steps:

First Step: The clay material was stirred and allowed to settle in a large beaker for a certain length of time. Then the clay particles of a depth at 10 cm (from the surface of water) were decanted into a porcelain filter. This was allowed to dry through evaporation in open air. In this way, a clay sample was obtained.

Second Step: The beaker which contained the remaining clay material was filled with water up to the original level. It was again stirred and allowed to settle for the same period of time as in the first step. Clay at the same depth (10 cm) was decanted away. The purpose of this step is to ensure that the clay particles extracted in the first step were entirely separated from the clay of larger size (which were still in the beaker).

For each clay sample, the same procedure consisting of these two steps was carried out on the remaining part of clay material after the previous extraction. Thus the clay particles became larger and larger as the separation analysis proceeded and the samples were accordingly graded from fine to coarse. The beaker was always filled with approximately the same amount of water. A constant depth of 10 cm was used to extract the clay. Only the time of clay settlement was varied in order to obtain different particle sizes (Table 7).

No dispersion agent was added since every attempt was made to protect the sample from being contaminated. Thus the clay was not truly dispersed. Consequently the sizes of clay particles could not be calculated from usual sedimentation formulae.

Table 7. Clay separation analysis

Sample No.	Time of Clay Settlement	"Size"
N-4-1.	12 hours	finest
N-4-2	8 hours	
N-4-3	4 hours	
N-4-4	1 hour	
N-4-5	last portion*	coarsest

*N-4-5 was directly extracted from the last portion of the clay material after the coarsest fraction (which might have contained some mineral) had been carefully washed away.

Mineral Separation

The bulk of the mineral fraction was subjected repeatedly to the same clay cleaning treatment until finally a mineral fraction consisting primarily of biotite, quartz, sanidine, etc., was obtained. This assemblage of minerals, after being dried, was then sieved into three mesh-size fractions: 45-80 mesh, 80-170 mesh and < 170 mesh. In each mesh size fraction all the minerals were generally present. The problem was then to separate them into as pure as possible mineral phases.

Biotite was separated from non-magnetic minerals such as quartz, sanidine, etc., by employing a Frantz isodynamic separator. It was purified further by the same instrument with different and increasing currents and by employing heavy liquids. Bromoform and tetrabromo-ethane, either pure or diluted with acetone, were used. Methylene iodide was also necessary to separate biotite from garnet and pyrite. However, the biotite of fine-mesh size fraction ($<$ 170 mesh) could not be purified completely by the method of heavy liquids only. The final purification was carried out by rolling the impurity (pyrite, some oxidized garnet and magnetite) out on a piece of paper. Biotite, within a mesh size fraction, was finally graded by different specific gravities in tetrabromo-ethane mixed with acetone in various proportions (for a general description see Table 8).

Sanidine (from 80-170 mesh) was separated at 1° tilt and amperage of 1 ampere on a Frantz magnetic separator. The sanidine with specific gravity of 2.57 was very difficult to isolate from quartz (sp. gravity = 2.66) and some kaolinized plagioclase. After trying to separate the sanidine as pure as possible by using the heavy liquid method, it was washed with 6N hydrochloric acid. The cloudy solution was decanted away. The remaining part consisted mainly of sanidine and a few grains of quartz. At this stage, hand picking was carried out in order to obtain sanidine with the least impurity.

Apatite was extracted from the fraction smaller than 170 mesh and obtained as a pure sample by using heavy liquids. The apatite having a specific gravity from 3.15 to 3.20 sank in tetrabromo-ethane and floated in methylene iodide.

Calcite was obtained by hand picking from fossil remnant shells in the coarsest grit fraction.

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Table 8. Mineral Separation Data

Mineral	Mesh Size Fraction	No. Sample	Impurity per cent	Density	Descriptions
Biotite	45-80	N-1-1	none	heavy	unaltered
		N-1-2	none		
		N-1-3	2	light	partly altered
Biotite		N-2-1	1	heavy	unaltered
		N-2-2	1		
		N-2-3	2-3		
		N-2-4	2-3	light	partly altered
Biotite	< 170	N-3	2-3	heavy	
		N-3-1	"		unaltered
		N-3-2	"		
		N-3-3	"		
		N-3-4	5-10		
		N-3-5	10-20		
		N-3-6	10-20	light	partly altered
Apatite	< 170	N-10	none		
Sanidine	80-170	N-11	negligible		
Whole Bentonite		N-12			
C L A Y		N-4-1		fine	mixture of montmorillonite and illite with no difference in d-spacing from X-ray diffraction
		N-4-2			
		N-4-3			
		N-4-4			
		N-4-5		coarse	of fine to coarse samples.
Calcite	45-80	N-19	none		

APPENDIX 3

ANALYTICAL METHODS FOR Rb-Sr AGE DETERMINATION

Sample Preparation

After being purified the sample was ground to a fine powder in an agate mortar. The Sr and Rb contents of rock and mineral samples were estimated by X-ray fluorescent analysis. These estimates were utilized to give suitable amounts of samples to be mixed with quantitatively known Rb and Sr isotopic tracers ("spikes").

Rubidium: An approximate amount of sample to give Rb^{87}/Rb^{85} close to 2 in the spiked mixture was weighed into a platinum dish. A few drops of demineralized water, 5 ml of HF, five drops of H_2SO_4 and a precalibrated Rb spike were added to it. The sample was decomposed by heating on a hot plate and evaporated to dryness. The residue was heated to fumes of H_2SO_4, ignited over a Meeker burner for 30 minutes and allowed to cool. It was then warmed gently, leached with 2 ml. of water and transferred to a small glass vial. The leachate was evaporated to dryness and stored.

Strontium: An amount of sample to give about 10 μgm to 15 μgm of total strontium was weighed into a teflon beaker. The sample was moisten with water and 10 ml of HF, a 10 ml of redistilled 1 : 1 HNO_3 were added. The solution was allowed to dry slowly at a temperature of 100-120°C. The residue was then moistened with demineralized water and 5 ml of 1 : 1 HCl were added. The evaporation and baking were repeated. The residue was finally taken up in a minimum amount of 2.5 N HCl, transferred to a centrifuge tube and centrifuged to settle out any insoluble material. This small solution (less than 2 ml) was passed through a calibrated ion-exchange column. The Sr fraction was collected in a small glass beaker, evaporated to dryness and stored.

The spiked Sr samples were prepared in the same way except for the addition of the Sr tracer (or Sr spike).

A second method partially different from the previous one was also used to prepare some of the samples. Sufficient amount of sample to give convenient Rb

and Sr ratios was weighed into a teflon beaker and moistened with demineralized water. The same kinds of acid and of treatment (evaporation, baking etc.) were employed as in the first method. All of the final residue was completely brought into a solution of 25 ml demineralized water and 25 ml of 2.5 N HCl. Appropriate amounts of this liquid were pipetted out and mixed with Rb spike and Sr spike separately. The remaining solution was used as Sr unspiked. The Sr spiked mixture and the Sr unspiked solutions were then evaporated, taken up in centrifuge tubes, centrifuged and passed through ion exchange columns. The Sr fraction was collected in a small glass beaker, evaporated to dryness and stored.

The Rb spiked-mixture solution was also subjected to the same treatment described for Rb in the first method except that the addition of HF was clearly unnecessary here (since the sample was already completely decomposed and brought into solution).

Thus the second method differs from the first one in this, that the sample is first brought into solution and <u>then divided</u> into small proportions for the purpose of mixing with Rb and Sr tracers separately.

Special treatment for clay and fine biotite

It was observed that the clay samples did not completely dissolve in acids, even in HF alone or in a succession of HF, HNO_3 and HCl. In order to obtain an entire decomposition of the clay, it was dehydrated in an oven at 350°F for one hour and ignited over a Meeker burner for half an hour. Thus organic matter, if present in the sample, was eliminated to a certain extent and the clay became somewhat reddish brown since ferrous iron was transformed to ferric iron. After the ignition, the clay was treated with the same acids as used for other samples. However, the clay tended to give a big residue to be taken up in 2 ml. centrifuge tube.

The very fine biotite (less than 170 mesh) was also found to dissolve in acids with difficulty, therefore it was treated in the same manner as the clay.

Reagents and apparatus

All the teflon beakers, glass ware, cover lids, stirring rods used had been washed with detergent, rinsed with demineralized water and heated in 1 : 1 hydrochloric acid at about 350°F for more than three hours. Dry and clean beakers, centrifuge tubes and glass vials were wrapped with Parafilm and stored for use. Water was distilled and demineralized. Platinum dishes and crucibles (needed for Rb preparation) were heated in concentrated nitric acid for at least 2 hours and then ignited ($\approx$900°C). This cleaning procedure was carried out three times.

Nitric and hydrochloric acids were redistilled in a fused quartz distillation flask. Redistillation was not necessary for hydrofluoric and sulfuric acids.

Measurement of the isotopic ratios

Single tantalum filaments were used to load Rb and Sr samples. The filaments were heated to incandescence and degassed for approximately 2 to 3 hours in vacuum to remove any contaminant. The filaments were removed from the vacuum chamber and oxidized at atmospheric pressure before the samples were placed on them.

The Rb sample was taken into a fine-bore glass capillary tube with demineralized water and transferred to the tantalum filament. The filament was electrically heated (about 1 ampere) to dry the sample and then loaded directly into the mass spectrometer. Rb emission ordinarily began at a filament current of more than 1.0 ampere and measurable emission was usually obtained at 1.2 – 1.5 amperes, K^{39}/K^{41} ratios were measured together with Rb^{87}/Rb^{85} ratios to correct for mass discrimination. The K^{39}/K^{41} ratios were normalized to 13.71 and the Rb^{87}/Rb^{85} ratios were corrected by one half of the K correction.

The Sr samples were loaded on tantalum filaments in the same way as Rb. The filaments were then put back into the vacuum system, where the pre-treatment was carried out at a current of approximately 2 amperes for about 6-12 hours before being loaded into the mass spectrometer. This pre-treatment served to remove the alkali metals

from the sample and so increase the Sr emission. Sr emission ordinarily began at a filament current of 2.1 - 2.2 amperes and measureable ratios were usually obtained at a current of 2.3 - 2.5 amperes.

For the spiked samples, relative Sr^{88}, Sr^{87}, Sr^{86} and Sr^{84} abundances were measured. Mass discrimination was corrected by an iterative procedure using Sr^{88}/Sr^{86} and Sr^{84}/Sr^{86} ratios. An example to illustrate the method is shown on page 49. For the unspiked samples, relative Sr^{88}, Sr^{87} and Sr^{86} abundances were measured. Mass discrimination was corrected by normalizing the Sr^{86}/Sr^{88} ratio to 0.1194 (Nier, 1950) and correcting the Sr^{87}/Sr^{86} by one half the Sr^{86}/Sr^{88} correction.

All isotopic measurements were made on a 6-inch 60-degree deflection solid source mass spectrometer with a single filament source and a single collector cup. Most of the Rb and Sr runs were recorded on a chart recorder, some by an integrating digital voltmeter. When using the chart recorder, at least six spectra with highest stability of the run were taken and used for the calculation of isotopic ratios. Chart reading and the desired isotopic ratios were operated at every half of an inch on the chart. The final ratio was obtained by averaging these ratios. The instrument and/or reading error was expressed as standard deviation. When using the digital voltmeter, only one pair of peaks (Sr^{88} and Sr^{86}, Sr^{87} and Sr^{86}, Sr^{84} and Sr^{86}) were measured at a time as a set. The mass spectrometer scan was adjusted to the top of peaks and then switched from peak to peak by changing the magnet current. A minimum time of four seconds was necessary for the instrument to adjust from the top of the first peak to that of the second. The digital voltmeter integrated the instrument output over one second and printed the results on a chart paper. The chart recorder was used to follow the mass spectrometer output simultaneously and ensure that the top of the peaks were correctly recorded. Twenty measurements or more were made for each peak in the set. Being highly sensitive and accurate, the digital voltmeter, when used, required more stable emission than the chart recorder.

The isotopic ratios were calculated from the digital voltmeter results by averaging 2 measurements on the top of one peak and dividing by the measurement of the second peak. Thus each measurement of a peak is used three times in this way of calculation.

Example of calculation

Throughout the calculation mass discrimination is calculated as

$$\% \text{ M.D.} = 1 \pm \frac{(\text{value})_{\text{meas.}}}{(\text{value})_{\text{adopted}}} \times 100$$

with the convention that M.D. has sign (-) when $(\text{value})_{\text{meas.}} < (\text{value})_{\text{adopted}}$ and sign (+) when $(\text{value})_{\text{meas.}} > (\text{value})_{\text{adopted}}$.

Sample N-2-3 Biotite

Measured atomic ratios:

$$K^{39}/K^{41} = 13.65 \text{ normalized to } 13.71 \text{ where M.D.} = -.44\%$$

$$(Rb^{87}/Rb^{85})_{\text{meas.}} = 1.3690$$

$$(Rb^{87}/Rb^{85})_{\text{norm.}} = (Rb^{87}/Rb^{85})_{\text{meas.}} \times (1 - \text{M.D.}/2)$$

$$= 1.3660$$

In Sr spiked run:

$$(Sr^{88}/Sr^{86})_{\text{meas.}} = 2.3074$$

$$(Sr^{87}/Sr^{86})_{\text{meas.}} = 0.2780$$

$$(Sr^{84}/Sr^{86})_{\text{meas.}} = 0.4371$$

In Sr unspiked run:

$$(Sr^{86}/Sr^{88})_{\text{meas.}} = 0.1188 \text{ normalized to } 0.1194 \text{ (Nier, 1950);}$$
$$\text{M.D.} = -.50\%$$

$$(Sr^{87}/Sr^{86})_{\text{meas.}} = 0.8997$$

$$(Sr^{87}/Sr^{86})_{\text{norm.}} = (Sr^{87}/Sr^{86}) \text{ meas.} \times (1 - \text{M.D.}/2)$$

$$= 0.89745$$

Rubidium:

Knowing

$$\text{spiked composition } Rb^{87}_{85} = 20.745 \,\mu gm$$
$$Rb^{85} = 0.165 \,\mu gm$$

$$\text{normal Rb composition } Rb^{87}_{85} = 27.85 \,\%$$
$$Rb^{85} = 72.15 \,\%$$

wt. of sample Rb spiked = 0.06973 gm

$$(Rb^{87}/Rb^{85})_{norm.} \times 87/85 = \frac{\mu gm \ Rb^{87} \ sp + \mu gm \ Rb^{87}N}{\mu gm \ Rb^{85} \ sp + \mu gm \ Rb^{85}N}$$

$$1.3660 \times 87/85 = \frac{20.745 + \mu gm \ Rb^{87}N}{0.165 + \mu gm \ Rb^{85}N}$$

as $\mu gm \ Rb^{85}_{N} = 2.530 \,\mu gm \ Rb^{87}_{N}$ $\mu gm \ Rb^{87}_{N} = 8.0853$

then ppm $Rb^{87} = \mu gm \ Rb^{87}/\text{sample wt.} = 409.303$

Strontium:

$$(Sr^{88}/Sr^{86})_{meas.} \times 88/86 = \frac{\mu gm \ Sr^{88} \ sp + \mu gm \ Sr^{88}N}{\mu gm \ Sr^{86} \ sp + \mu gm \ Sr^{86}N}$$

but knowing $Sr^{88}_{sp.} = 1.406 \,\mu gm$

$$Sr^{87}_{sp.} = 0.3835 \,\mu gm$$

$$Sr^{86}_{sp.} = 5.592 \,\mu gm$$

$$Sr^{84}_{sp.} = 3.107 \,\mu gm$$

$Sr^{88}_{N} = 0.8283 \ Sr_{N}$ total and $Sr^{87}_{N} = 0.967 \ Sr_{N}$ total

using these substitutions and solving for Sr_{N} total:

Sr_{N} total = 19.66 μgm in 0.55906 gm of sample

$$(Sr^{84}/Sr^{86}) \text{ calculated} = \frac{(0.0054 \times 19.66) + \mu gm \ Sr^{84}spike}{(0.0967 \times 19.66) + \mu gm \ Sr^{86}spike}$$

$$= 0.4288$$

Comparing this with $(Sr^{84}/Sr^{86})_{meas.}$ converted to weight ratio by multiplying with 84/86, the M.D. is obtained as follows:

$$M.D. = 1 - \left[\frac{(Sr^{84}/Sr^{86})_{meas.} \times 84/86}{(Sr^{84}/Sr^{86}) \text{ calculated}} \right] \times 100$$

$$= -0.44\%$$

The negative mass discrimination indicates that more of the lighter atoms have been removed by fractionation than heavier atoms. Consequently, the $(Sr^{88}/Sr^{86})_{meas.}$ ratio is too high. To correct for this mass-discrimination effect the $(Sr^{88}/Sr^{86})_{meas.}$ is multiplied by 0.9956 (= 1-0.0044) and the Sr_N^{total} is recalculated using this value. This procedure is repeated until the Sr_N^{total} does not change. In this example, the calculation has been repeated four times.

The results obtained are:

$Sr_N^{total} = 19.47\,\mu gm/$in 0.55905 gm of sample   M.D. = -0.65%

$$Sr^{87*} = \left[87/86 \times Sr^{87}/Sr^{86}_{meas.} \times \left(1 - \frac{M.D.}{2} \right) \times (Sr^{86}_N + Sr^{86}_{sp}) \right] - (Sr^{87}_N + Sr^{87}_{sp})$$

$Sr^{87*} = 0.3566\,\mu gm = 0.6379$ ppm

$$Sr^{87}/Sr^{86} \text{ (atomic ratio)} = \left[\frac{\text{ppm } Sr^{87}_N + \text{ppm } Sr^{87*}}{\text{ppm } Sr^{86}} \right] \times \frac{86}{87} = 0.8987$$

$$Rb^{87}/Sr^{86} \text{ (atomic ratio)} = \frac{\text{ppm } Rb^{87}}{\text{ppm } Sr^{86}} \times \frac{86}{87} = 34.03$$